

# Binary Gas Diffusion of Methane-Nitrogen Through Porous Solids

Diffusion rates of nitrogen and methane have been measured across ten porous solids at 35°C and 1 atm by a steady state flow method. The porous plugs used were cylindrical in shape, with diffusion occurring in the direction of the axis. Diffusion data were taken with porous cores either dry or saturated with liquids. Water and *n*-heptane were used as saturating liquids.

The rather complex internal structure of porous solids were indirectly characterized through some auxiliary measurements. These included porosity, permeability, and electrical resistivity factor (yet another indirect measurement of tortuosity).

The effective diffusion coefficients were correlated for the gas phase diffusion as a function of porosity. The ratio of effective diffusion coefficient to the open space diffusion coefficient ( $D_e/D_o$ ) was correlated for dry cores using the properties approximately characterizing the pore structure.

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## SCOPE

Rates of migration of fluids through porous and permeable sedimentary rocks in the crust of the earth occur through geological times being controlled by diffusional transport processes. Such phenomena are important in understanding the origin and occurrence of fossil fuels. Many other chemical engineering processes of current interest and relevance also relate to earth sciences. Underground storage of natural gas, compressed air storage for peak shaving, underground nuclear explosions, disposal of nuclear waste, in situ coal gasification are but a few examples of such operations in the forefront of present interest.

In many areas, drilling operations provide diverse samples of porous rock in the form of cores. These porous cores are complex consolidated porous matrices which provide the environment through which or into which oil and gas migrate. As such, they are quite different from unconsolidated granular solids such as packing materials, catalysts encountered in day to day chemical engineering operations.

As we embark upon new projects and processes related to fossil fuels and directed for generation of fuels or energy, in situ, it becomes particularly important that we have data on diffusional characteristics of the porous solids as they are encountered in the crust of the earth.

The most elementary measurements of porous rocks, describing their storage and transmissibility characteristics, are porosity and permeability. Because these rather simple measurements are not only widely available as data representing many different formations but also relate to the structure of porous matrix as well as to its transport properties, they were thought of as possible correlating parameters for effective diffusion coefficients.

This paper presents data on diffusion of methane and nitrogen across porous cores dry or saturated with water or normal heptane. Effective diffusion coefficients calculated from the data have been correlated against those properties of the porous media which determine their ability to store and transmit fluids.

## CONCLUSIONS AND SIGNIFICANCE

Diffusion of gases through porous media may be characterized by the same parameters which are known to describe the structure of the porous matrix and its transmissibility to fluid flow. These parameters are directly or indirectly measurable. They are porosity, permeability, and tortuosity. The latter is indirectly measured through the electrical resistivity factor. For dry porous solids, the effective diffusion coefficient measured for methane-nitrogen counterdiffusion appears to correlate reasonably well with the porosity of the porous medium.

For dry porous solids, the ratio of effective diffusion coefficient to open space diffusion coefficient ( $D_e/D_o$ ) correlates linearly on log-log plot with  $(1/F)$ , inverse formation resistivity factor. For dry porous solids, two alternate but approximately as valid correlations are given, one with permeability and the other with the permeability-porosity product. The effective diffusion coefficient data for nitrogen-methane across cores saturated with liquid

phase (water or normal heptane) indicate reduction of diffusion rates by a factor of 1 000. There is some suggestion from data on hand that swelling of native clays may be partially responsible for the drastic reduction indicated above.

The data on hand also indicate that the ratio of porous to open space diffusion coefficients for liquid saturated porous media correlate only approximately but reasonably over a log-log quadrant of 9 cycles by 3 cycles.

While the above correlations are admittedly subject to some scatter believed due to incomplete characterization of porous matrix, their present significance is through the data they contribute to the literature where such factors as permeability, porosity, and electrical resistivity factors are also available and given.

These data should permit at least some approximate calculations of diffusional rates across naturally occurring porous materials.

Diffusion coefficients have been measured and related to properties of interest for rocks of the earth, that is, permeability, porosity, and formation resistivity factor. Limited measurements of gas diffusion through water saturated rocks have been made in the USSR (Sokolob et al., 1963; Karstev, 1959). Pandey, Katz, and Tek (1974) and Chen (1973) made the only measurements known for diffusion of gas using both dry and liquid filled reservoir rocks.

The purpose of this study was to measure the effective diffusion coefficients for gases through dry and water filled porous media and to measure those properties which would describe the relevant characteristics of the porous matrix. The diffusion factor (the ratio of effective diffusion coefficient to the open space diffusion coefficient) characteristic of porous solids has been correlated as a function of resistivity factor, porosity, and permeability.

## EXPERIMENTAL WORK

The objective of experiments was to obtain data from which one could calculate the effective diffusion coefficients for nitrogen and methane through porous media. Parameters describing the tortuous structure of porous matrix, storage, and transmissibility of the fluids across were considered to be permeability, porosity, and formation resistivity factor. The permeability of the cores were calculated by Darcy's law (Katz et al., 1959). The porosity was measured by the weight difference between the dry and water saturated porous solid. The formation resistivity factor was determined by measuring the electrical resistivity of the porous solid saturated with 0.1 potassium chloride solution. A mass spectrometer was employed for determining gas compositions.

### Apparatus

The measurements of diffusion rates were made by the modified Wicke and Kallenbach (1941) method, in which nitrogen flowed across one face of the porous medium and methane flowed across the other. Thus, countercurrent diffusion occurred through the porous medium.

The apparatus for diffusion rate measurements is shown in Figure 1. The flow rate of gas was controlled by the needle valve of the micro flowmeter and the pressure in the gas supply. A soap bubble meter was connected at the outlet of a calibrated orifice meter, placed next to the micro flowmeter to calibrate the flow rate. The differential pressure between the two inlets of gas stream was measured by a water manometer. A liquid saturator was placed between the gas supplier and the diffusion cell when the diffusion rate of gas was measured through a water filled porous solid. The outlet of each side of the diffusion cell provided a sampling device which collected 50 ml of gas sample at 2 cm Hg pressure.

The diffusion measurement system was placed in a constant temperature air bath which was controlled at  $35^\circ \pm 0.5^\circ\text{C}$  by a bimetal thermoregulator.

### Diffusion Cell

The diffusion cell was made of plastic, which is practically resistant to all organic solvents, and had three parts. Two end parts were designed for gas influx and distribution of gas over the surface of the porous media. The middle part of the diffusion cell contained the porous medium. Six of the specimens had a 25 mm square cavity filled with glass beads or sand to a length of 5 cm. The beads were secured in position by a removable screen. The other four units were designed with a 38 cm diameter hole into which a sandstone core 1.38 cm long was fitted and cemented with epoxy. The ends of the sandstone had been ground to a smooth surface.

### Diffusion Measurements on Dry Porous Solids

After the assembled diffusion cell was placed in the apparatus, the system was checked for leaks with nitrogen at 225 k Pa (1.5 atm). The pure nitrogen and methane were turned on simultaneously. The flow rates of gases were controlled at a level high enough to preclude the effect of concentration of diffusing species in the gas stream. The pressure difference between the two inlet gas streams normally was held to  $\pm 2$  mm

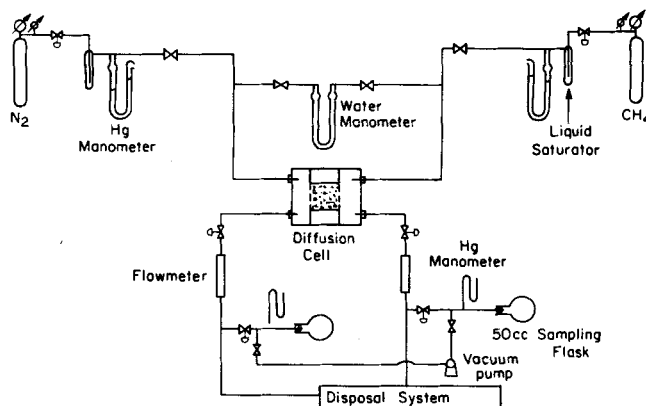


Fig. 1. Measurement system for diffusion rates.

water by adjusting the pressure of the gas supplier and the flow rates. Then, both nitrogen and methane side gas samples were taken consecutively to the mass spectrometer where the gas composition analyses were made. A steady state was reached when the values of calculated effective diffusivity became constant. In a typical experiment with the apparatus described above, it normally took 4 hrs. before steady state was reached. The measurements were continued for at least 2 days to ensure that steady state had been obtained and maintained.

The equation for describing the transfer rate of gas through a porous solid by the Wicke and Kallenbach method was developed by Evans, Watson, and Mason (1961):

$$N_A = -De \frac{PA}{RT} \frac{dY_A}{dz} + Y_A(N_A - N_B) \quad (1)$$

The integrated form of Equation (1)

$$De = \frac{N_A \alpha RTZ}{PA \ln \frac{1 - \alpha Y_{AZ}}{1 - \alpha Y_{A0}}} \quad (2)$$

was used to calculate the effective diffusion coefficients. The transfer rate of methane was calculated by the product of the increment of methane composition in the nitrogen stream and the flow rate of nitrogen. The transfer rate of nitrogen was calculated by the product of the increment of nitrogen composition in the methane stream and the flow rate of methane.

### The Diffusion Measurements Across Liquid-Filled Porous Media

The method of measuring diffusion through liquid filled consolidated porous media was similar to that for dry porous solids.

The sandstone (the middle part of the diffusion cell) was first saturated with liquid and then assembled. The pure nitrogen and methane were turned on simultaneously. Because the diffusion rate was very small, the flow rates of gases were maintained as low as possible to ensure that the gas composition was measurable. The gas samples of the nitrogen side were taken periodically for composition analysis by a mass spectrometer. The minimum time required to reach steady state was approximately 5 days. The measurements were continued for at least 10 days.

The diffusion coefficient of methane through liquid filled porous solids was calculated by the integrated Fick's first law rather than Equation (1). Because the threshold displacement pressure for liquid phase from the porous plug was not exceeded, the diffusional transport was taking place across a totally liquid environment:

$$N_B = - (De)_l A \frac{dC_B}{dz} \quad (3)$$

$$(De)_l = \frac{N_B Z}{A(C_{B2} - C_{B1})} \quad (4)$$

The mass transfer rate  $N_B$  was computed according to the number of moles of methane increased in the nitrogen stream. But the concentration difference ( $C_{B2} - C_{B1}$ ) in Equation (4) was computed in two ways: one was the concentration differ-

TABLE 1. SUMMARY OF EXPERIMENTAL RESULTS OF DRY POROUS SOLIDS AT 35°C, 1 ATM

Cell	Material	$\phi$	$K$ , Darcy	$F$	$\tau$	$De_i$ , cm <sup>2</sup> /s	$De$ , cm <sup>2</sup> /s	$Dem$ , cm <sup>2</sup> /s
1	3 mm GB random	39.6	25.3	4.02	1.26	0.0707	0.0784	0.0740
2	5 mm GB cubic	46.7	31.8	3.14	1.21	0.150	0.183	0.163
3	5 mm GB ortho-rhombic	41.4	26.3	3.95	1.25	0.156	0.200	0.173
4	5 mm GB random	39.9	28.2	3.98	1.26	0.0865	0.0983	0.0917
5A	Fine GB random	37.4	21.6	4.37	1.28	0.0567	0.0623	0.0592
6A	Sand	37.1	16.2	4.43	1.28	0.0652	0.0732	0.0685
7	Sandstone	14.1	0.0101	76.3	3.28	0.00333	0.00347	0.00340
8	Sandstone	11.7	0.00738	98.0	3.39	0.00259	0.00266	0.00262
9	Sandstone	12.7	0.049	61.6	2.54	0.00674	0.00725	0.00696
10	Sandstone	19.1	0.336	21.6	2.03	0.0103	0.0100	0.0106

$\phi$  = porosity %,  $K$  = permeability,  $F$  = electrical resistivity factor,  $\tau$  = tortuosity,  $De_i$  = diffusion coefficient by inlet gas streams,  $De$  = effective diffusion coefficient by outlet gas streams,  $Dem$  = effective diffusion coefficient by log-mean average of inlet and outlet gas streams.

ence of methane in the nitrogen and in the methane gas streams; the other was the concentration difference in the pore water at the surfaces of porous solids exposed to the nitrogen and to the methane gas streams.

The diffusion rates of methane through three partially water saturated and two fully water saturated sandstones were determined. Additionally, one set of experiments was conducted with the sandstone plug fully saturated with normal heptane. During the calculations, any mass transfer resistance at the end of the cell has been neglected.

**Results for Dry Porous Solids**

Table 1 shows the basic data on various porous cells and three computed effective diffusion coefficients. Of the basic data characterizing the porous medium, porosity, permeability, and electrical resistivity factor were directly measured. The tortuosity was computed.

The back diffusion effects on the diffusion coefficient are also shown in Table 1. For the unconsolidated diffusion cells, the average values of the difference between the values of the effective diffusivity calculated by the mole fractions of nitrogen in the outlet gas streams or in the inlet gas streams, or those calculated by the log-mean mole fraction of nitrogen in inlet and outlet gas streams, are within 10% of the calculated value. These

differences are about 4% of the calculated value for consolidated porous materials.

Since the pressure difference across the diffusion cell was very difficult to maintain at levels less than 1 or 2 mm water, the effects of forced flow on the effective diffusivities of dry porous solids were evaluated. When a differential pressure exists, the flux ratio of two species no longer obeys the law of inverse square root of molecular weight but varies as pressure difference changes. Figure 2 shows that  $De$  is not affected by the forced flow even when up to  $\pm 30$  mm of water for the differential pressure is used.

The structure of porous matrix is determined by the packing pattern, particle size and shape, and the nature of cementing agent. An unconsolidated diffusion cell is an idealized porous solid and is packed with glass beads of uniform size. Cubic and orthorhombic arrangements give two basic configurations of the interstices, cell numbers 2 and 3 as designated on Table 1. The interstices of both packing patterns provide relatively unblocked paths and give only a little hindrance to the diffusion process; that is, they yield a high effective diffusion coefficient.

The random packing is more like a packing pattern of consolidated reservoir rocks. The three randomly packed glass bead diffusion cells indeed show lower effective diffusivity. They also illustrate the effect of particle size on the effective diffusivity; that is,  $De$  decreases as particle size decreases. The data of diffusion cell No. 6A in Table 1 show the influence of the different sizes and shapes of particles contained in a typical sand pack.

**Results with Liquid Filled Sandstones**

The effective diffusivities of methane through liquid filled sandstones are given in Table 2. They were calculated by two

TABLE 2. SUMMARY OF RESULTS FOR METHANE DIFFUSION IN LIQUID FILLED SOLIDS AT 25°C, 1 ATM

Diff. cell No.	Liquid	% sat.*	$(De)_{gl}$ gas phase conc., cm <sup>2</sup> /s	$(De)_{ll}$ liq phase conc., cm <sup>2</sup> /s
7	Water	66.2	$2.41 \times 10^{-5}$	$8.33 \times 10^{-4}$
8	Water	29.6	$1.17 \times 10^{-3}$	$4.06 \times 10^{-2}$
9	Water	89.7	$1.33 \times 10^{-3}$	$4.61 \times 10^{-3}$
9	Water	100.0	$1.43 \times 10^{-6}$	$4.98 \times 10^{-5}$
10	Water	100.0	$3.38 \times 10^{-6}$	$1.17 \times 10^{-4}$
7	<i>n</i> -heptane	100.0	$2.04 \times 10^{-6}$	$3.01 \times 10^{-6}$

Open Space Diffusivity at 35°C, 1 atm:

$D_{gl} = 2.12 \times 10^{-5}$  cm<sup>2</sup>/s for methane in water (19)

$D_{gl} = 8.50 \times 10^{-5}$  cm<sup>2</sup>/s for methane in *n*-heptane (20)

\* The first runs on diffusion cell Nos. 7, 8, 9 were intended to be fully saturated throughout the test. A check on the weight of cell before and after along with porosity revealed the water loss during measurement. The saturator was transferred to the higher temperature as a corrective measure.

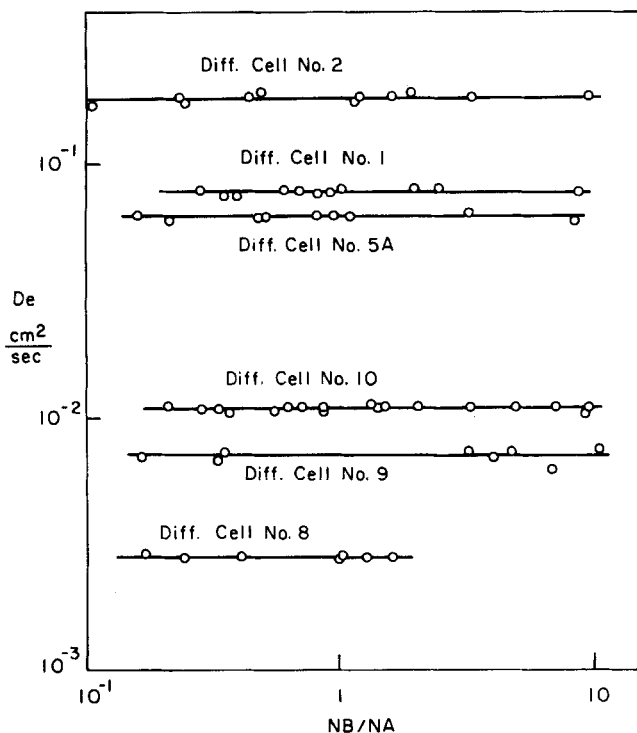


Fig. 2. Effective diffusivity vs. flux ratio (dry).

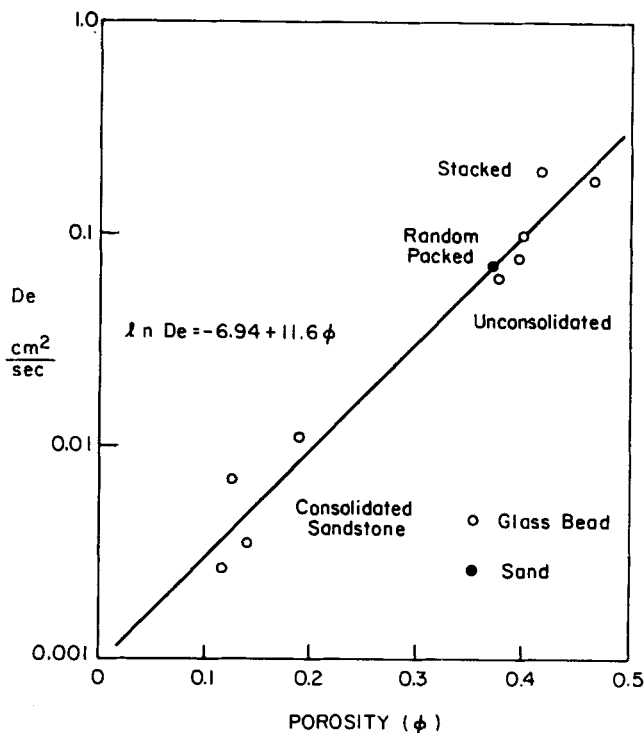


Fig. 3. Effective diffusion coefficient vs. porosity for dry porous solid.

methods: one, the concentration difference in Equation (4) was taken as the difference in free gas phase concentration at either end. The other,  $(De)_{11}$ , was calculated by using the concentrations of the diffusing component in the liquid phase. These methane concentrations in the liquid phase, prevailing in surface pores at both ends of the diffusion cell, were calculated by using Henry's law constant for the methane-water system and Ostwald absorption constant for methane-*n*-heptane system. Table 2 shows that the values of effective diffusivities of methane through liquid filled sandstones calculated on the basis of liquid phase concentrations are higher by an order of magnitude than the values calculated on the basis of free gas phase concentrations.

**CORRELATIONS**

Two different types of correlations were developed in the course of this work. First, the diffusion coefficients themselves were correlated with porosity. Second, the ratio of  $De/D_o$ , the diffusion coefficient across the solid to the diffusion coefficient across open space, was correlated against factors describing the solid interstices. The value of  $D_o$  used in this study was  $0.227 \text{ cm}^2/\text{s}$ . It was calculated from the procedure given by Hirschfelder, Bird, and Spatz (1949).

The effective diffusion coefficient is correlated with porosity as shown in Figure 3. The scattering of data from the correlated curve is due to the incompleteness of the parameter  $\phi$  as a full descriptor of the interstices with regard to diffusion.

The ratio of  $De/D_o$ , the diffusion coefficient across the solid to the diffusion coefficient across open space, describes the character of the porous matrix. The formation resistivity factor, which is defined as the ratio of the electrical resistance of a volume of brine filling the existing pore structure to that of an equivalent volume of brine filling void space of same overall dimensions, also characterizes the structure of the porous matrix. Accordingly  $De/D_o$  was plotted against the inverse of the formation resistivity factor ( $1/F$ ) in a log-log scale as shown in Figure 4.

Also shown in Figure 4, the data by Donaldson, Kendall, and Manning (1976) take on hydrogen-air and

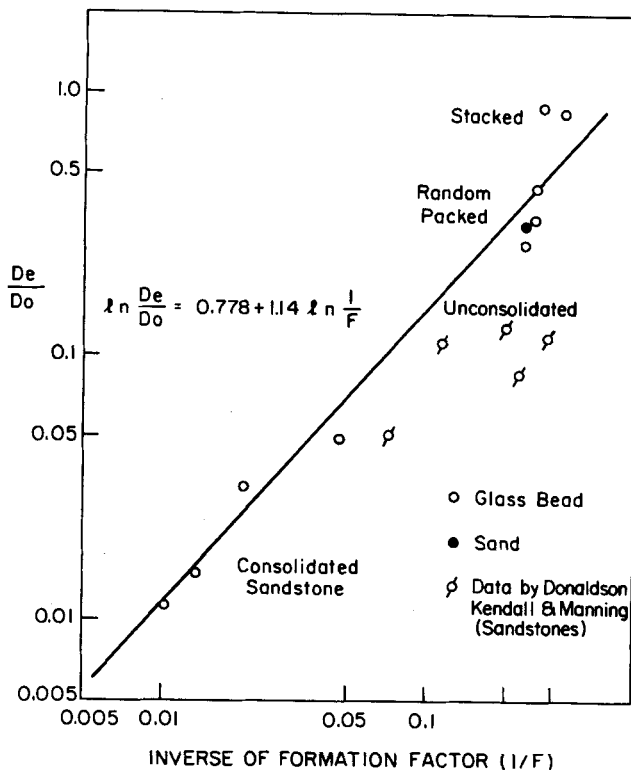


Fig. 4. Diffusion factor vs. inverse of formation resistivity factor for dry porous solid.

hydrogen-nitrogen systems using five different sandstone cores. Donaldson et al. used samples having immobile fluid fractions and a tritium tracer dispersion technique to calculate the effective diffusivities. The fact that their data fell significantly below the correlation developed in this work may be attributed to the presence of immobile brine phase and possible interaction of the tracer with their connate phase.

In order to see whether a general relationship exists between effective diffusivity and permeability for all kinds of gas systems and low permeability cores, a plot of  $De/D_o$  vs. permeability ( $K$ ) has been made with the data of this study and the data of Pandey, Katz, and Tek (1974) in their investigation of helium-nitrogen diffusion through reservoir rocks. Figure 5 shows that the diffusion factor ( $De/D_o$ ) is also linearly proportional to permeability in logarithmic scale from  $10^{-8}$  to  $3.18 \times 10^1$  Darcies. Also shown in Figure 5 are the data from Donaldson et al. with reasonable agreement with the correlation developed in this work.

The fundamental knowledge on unsteady state fluid flow through porous media suggests that effective diffu-

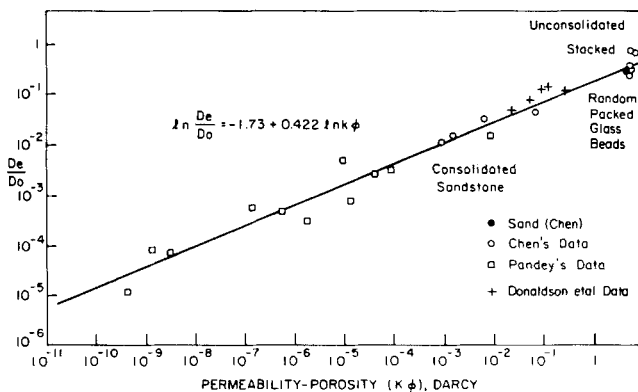


Fig. 5. Diffusion factor vs. permeability for dry porous solid.

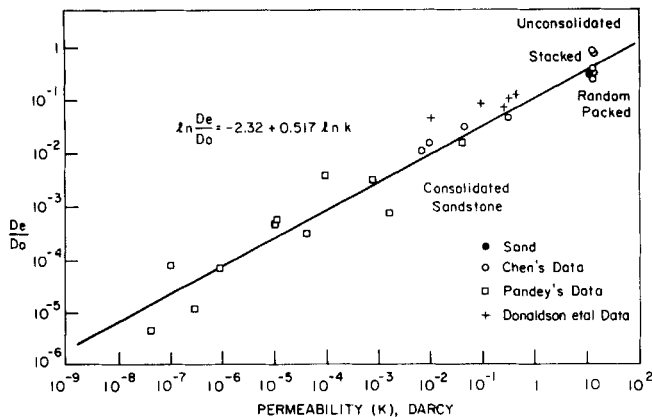


Fig. 6. Diffusion factor vs. permeability-porosity product for dry porous solid.

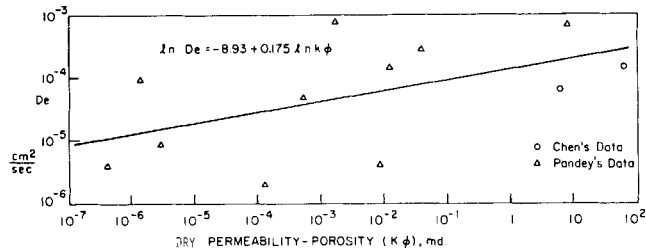


Fig. 7. Effective diffusion coefficient vs. dry permeability-porosity product for water saturated porous solids.

sivity may be affected by porosity as well as permeability. For practical reasons and because of the need for at least an approximate correlation, the diffusion factor  $De/Do$  was correlated with the product of permeability and porosity as shown in Figure 6 for both data of Chen (1973) and Pandey, Katz, and Tek (1974). Again, for comparison, the data of Donaldson et al. are shown to be in reasonably good agreement with the correlation developed.

The data of this study for water saturated sandstones were multiplied by a correction factor of temperature and molar volume of solute corresponding to the values of effective diffusion coefficients for helium. They were then combined with the data of Pandey, Katz, and Tek (1974); a plot of effective diffusivities through water saturated cores vs. the (dry) permeability-porosity product ( $K\phi$ ) is shown in Figure 7. The scatter of the data

is believed due in part to the uneven changes in pore structure from the dry state for permeability measurements to wet state for diffusion measurements. Even though the correlating line is very approximate, the range it covers (9 cycles  $\times$  3) should still permit some meaningful calculations for diffusional processes in geological time scale.

## DISCUSSION OF RESULTS

Diffusion factor  $(De/Do)_{gl}$ , the ratio of the effective diffusion coefficient, based on free gas phase concentration for liquid saturated cores, to the diffusivity of gas in open space liquid is computed and given in Table 3. The values of  $(De/Do)_{gl}$  are in the same order of  $De/Do$  of corresponding dry porous solids.

$(De/Do)_u$  the ratio of the effective diffusion coefficient of liquid saturated cores, based on the liquid phase concentration, to the diffusivity of gas in open space liquid is also given in Table 3. For methane-*n*-heptane system,  $(De/Do)$  is in the same order but with higher magnitude than the value of  $(De/Do)$  for the corresponding dry core. The values of  $(De/Do)_u$  for methane-water system are approximately 100 times greater than the values of  $(De/Do)$  of the corresponding dry cores.

Data of  $(De)_u$  indicate that for methane-water system, the diffusion of methane through a water saturated core into nitrogen was faster than diffusion in open space filled with water. Similar results were also obtained by Pandey, Katz, and Tek (1974) for the diffusion of helium through water saturated caprocks. On the other hand, the diffusion of methane through an *n*-heptane saturated core was hindered by the presence of a porous medium. If there were some error in these two studies which accounted for the higher diffusion across porous media than across pure bulk liquids, it would have had to have been one of the following: the analytical method, the presence of nitrogen in counterdiffusion, the core holder, and the procedure of using Henry's law for calculating the concentration of the gas dissolved in the water. Since the diffusion rate in the porous solids is too high in comparison with the bulk liquid, there is no indication of a lack of equilibrium between the gas and the water interface. A reexamination of these factors does not indicate that there have been errors of the

TABLE 3. COMPARISON OF DIFFUSION FACTOR FOR DRY AND LIQUID SATURATED POROUS SOLIDS

Diff. cell No.	$\phi$ , %	K, Darcy	F	$\left(\frac{De}{Do}\right)_{dry}$	$\left(\frac{De}{Do}\right)_{gl}$	$\left(\frac{De}{Do}\right)_u$
7	14.1	0.0101	76.3	0.0153	0.0240	0.0354*
9	12.7	0.049	61.6	0.0319	0.0674	2.34†
10	19.1	0.336	21.6	0.0484	0.0159	5.54†
Data of Pandey, Katz, and Tek						
1	4.95	$1.1 \times 10^{-5}$	1 629.5	$4.71 \times 10^{-4}$	—	0.698
2	0.30	$1.0 \times 10^{-6}$	1 260.0	$6.68 \times 10^{-5}$	—	0.138
3	1.08	$1.19 \times 10^{-5}$	1 109.0	$5.61 \times 10^{-4}$	—	0.0306
4	18.70	$4.48 \times 10^{-2}$	54.2	$1.61 \times 10^{-2}$	—	10.8
5	0.73	$1.725 \times 10^{-3}$	139.0	$7.66 \times 10^{-4}$	—	2.35
6	0.13	$3.26 \times 10^{-7}$	2 326.7	$1.14 \times 10^{-5}$	—	0.0635
7	3.95	$4.5 \times 10^{-5}$	1 650.0	$3.09 \times 10^{-4}$	—	12.05
8	10.20	$8.1 \times 10^{-4}$	728.8	$3.12 \times 10^{-3}$	—	—
9	9.51	$9.25 \times 10^{-5}$	—	$4.86 \times 10^{-3}$	—	0.0652
10	1.34	$1.05 \times 10^{-7}$	499.0	$7.92 \times 10^{-5}$	—	1.52
11	0.00	$4.41 \times 10^{-8}$	1 090.0	$4.49 \times 10^{-6}$	—	—
12	5.60	$7.07 \times 10^{-4}$	160.0	$2.56 \times 10^{-3}$	—	4.39

\*  $\beta = 0.6768$  for methane-*n*-heptane system at 35°C and 760 mm Hg.

†  $H = 36.95 \times 10^6$  mm Hg for methane in water at 35°C and 760 mm Hg.

TABLE 4. COMPARISON OF DIFFUSION RATE OF METHANE ( $N_B$ ) THROUGH DRY AND LIQUID SATURATED SANDSTONES

Diff. cell No.	$(N_B)_{dry}$ mole/s	$(N_B)_{liq-sat}$ mole/s	$\frac{(N_B)_{dry}}{(N_B)_{liq-sat}}$
7	$1.2 \times 10^{-6}$	$6.5 \times 10^{-10}$	$1.85 \times 10^3$
9	$3.0 \times 10^{-6}$	$4.7 \times 10^{-10}$	$6.39 \times 10^3$
10	$2.0 \times 10^{-6}$	$6.95 \times 10^{-9}$	$0.29 \times 10^3$

Theoretical values of  $\frac{(N_B)_{dry}}{(N_B)_{liq-sat}}$

$3.95 \times 10^3$  for  $CH_4$  in *n*-heptane  
 $3.73 \times 10^5$  for  $CH_4$  in water

TABLE 5. COMPARISON OF GAS AND WATER PERMEABILITY OF DIFFUSION CELL NO. 9 AND NO. 10

Diff. cell No.	Gas permeability, Darcy	Water permeability, Darcy
9	0.049	0.0025
10	0.336	0.0713

magnitude indicated by the results reported on Table 3, and the matter still remains an unanswered question.

**Comparison of Diffusion Rate of Methane Through Dry and Liquid-Saturated Sandstones**

The rates of diffusion of methane through dry and liquid saturated sandstones are presented in Table 4. The data show that the presence of liquid in the pores of sandstone reduces the rate of methane diffusion across the porous medium by an approximate factor of  $10^3$ .

Theoretically, the ratio of the diffusion rate of methane through dry and liquid saturated porous medium could be represented by the following equation:

$$\frac{(N_B)_{dry}}{(N_B)_{liq-sat}} = \frac{D_{12}}{D_{gl}\beta} \quad (5)$$

The results show that the methane-*n*-heptane system is close to the theoretical value, but the methane-water system is much lower than the theoretical system. Water is believed to cause interstices of the cores to change shape by swelling the clay, while *n*-heptane does not cause such swelling. Water permeability was measured for diffusion cell No. 9 and No. 10 and given in Table 5. The results indicated that the water permeability was much lower than the gas permeability. The lowered water permeability is believed due to the swelling by water of the clay type of material in the core, creating a different pore structure.

Since the pore structure is changed and represents a new porous medium with respect to the interstices, it can be expected that the diffusion results in dry mode and in water saturated mode will be different, as compared to open space.

**NOTATION**

- A = area of cross section,  $cm^2$
- C = concentration, mole/ $cm^3$
- De = effective diffusion coefficient,  $cm^2/s$  (calculated by the concentration of outlet gas streams)
- Dei = effective diffusion coefficient,  $cm^2/s$  (calculated by the concentration of inlet gas streams)

- Dem = effective diffusion coefficient,  $cm^2/s$  (calculated by the concentration of log-mean average of outlet and inlet gas streams)
- Dei = effective diffusivity of liquid filled porous media,  $cm^2/s$
- (De)<sub>gl</sub> = effective diffusion coefficient of liquid filled porous media,  $cm^2/s$  (calculated by the concentration difference in adjacent free gas phases)
- (De)<sub>u</sub> = effective diffusion coefficient of liquid filled porous media,  $cm^2/s$  (calculated by the concentration difference in liquid phases)
- De/Do = diffusion factor, diffusivity in porous solid over diffusivity in open space
- F = formation resistivity factor
- H = Henry's law constant
- K = permeability, Darcy
- N = molar diffusion rate, mole/s
- P = pressure, cm Hg
- R = gas constant
- T = absolute temperature, °K
- Y = mole fraction in gas phase
- z = distance, cm
- Z = length of porous medium, cm
- $\alpha = 1 - N_B/N_A$
- $\beta$  = Ostwald absorption coefficient, concentration in liquid phase over concentration in gas phase
- $\phi$  = porosity
- $r$  = tortuosity

**Subscripts**

- 1 = nitrogen, or nitrogen side chamber, or liquid
- 2 = methane, or methane side chamber
- A = nitrogen
- B = methane
- e = effective
- g = gas

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